Enhancement of proton exchange membrane fuel cells performance at elevated temperatures and lower humidities by incorporating immobilized phosphotungstic acid in electrodes

Anima B. Bose*, Susmitha Gopu [1], Wei Li

Department of Engineering Technology and Texas Center for Superconductivity, University of Houston, Houston, TX 77204, USA

HIGHLIGHTS

- Adding PWA/SiO$_2$ both in the membrane and electrodes increases the MEA performance.
- The proton conductivities in the electrodes increase.
- The proton transport across the membrane/electrode interfaces increases.
- Immobilized PWA/SiO$_2$ in the electrodes does not poison the electrocatalysts.

ARTICLE INFO

ABSTRACT

Doping phosphotungstic acid immobilized by silicon dioxide (PWA/SiO$_2$) in a Nafion membrane is an effective way to achieve a good proton conductivity of the membrane in proton exchange membrane fuel cells (PEMFCs) at elevated temperatures and lower humidity. To further advance the theory, immobilized PWA/SiO$_2$ was incorporated in the Nafion ionomer as the binder and proton conductor in the electrode matrices for additional performance enhancement. Two sets of membrane electrode assemblies (MEAs) were prepared and tested by incorporating PWA/SiO$_2$ both in the membrane and electrodes (MEA-1) and only in the membrane (MEA-2). Analyses of the ohmic resistance, open circuit voltage, Tafel slope, charge transfer time constant of the two MEAs indicate that the superior performance of MEA-1 at elevated temperatures and low relative humidities was primarily ascribed to a better hydration of electrodes. The protonic transports across the interfaces between the electrodes and membrane were also improved, which has less impact on the performance enhancement. These results also show that the immobilized PWA/SiO$_2$ in the electrodes did not exhibit poisoning effects on the electrocatalysts. The lack of poisoning effects is attributed to the stabilization of PWA in ionic channels with Nafion ionomer which does not interact with the electrocatalysts.

© 2014 Published by Elsevier B.V.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are known for their ability to generate electric power at high efficiencies via the electrochemical reaction between H$_2$ and O$_2$ gases. The state-of-the-art PEMFCs power sources are ready to enter the market places for a variety of applications. For instance, PEMFCs are a viable substitution for internal combustion engines as they fulfill conditions such as high power density, compact size, quick start-up time, and show promise for achieving cost-efficiency [1]. Perfluorosulfonic acid ionomer (Nafion®) is the benchmark proton exchange material for the proton exchange membranes (PEMs) and electrode binders used in PEMFCs [2]. This ionomer has high proton conductivity at high levels of hydration due to vehicular mechanism and Grotthuss mechanism [2,3]. However, its proton conductivity has a strong dependence on the water content, which limits its performance at elevated operating temperatures, especially above 80 °C due to its evaporation leading to a sharp drop in proton conductivity [2].

There are significant benefits for operating PEMFCs at higher temperatures and hence tremendous focus has been given over last decade on operating them under non-humidified conditions [4–6]. For example, raising the operating temperatures of PEMFCs offer

higher activities of electrocatalysts, higher CO tolerance of anode electrocatalysts, easier and more efficient water management, and faster heat rejection rates, etc. [4–6]. Also, higher temperature operations minimize the system complexities by reducing some components in power generating scheme. Higher operating temperatures of PEMFCs will reduce size and number of radiators in vehicles as the temperature difference between the engine compartment and power source decreases [4]. Hence, to enable the use of Nafion ionomer at elevated temperatures, it requires modification to attain suitable proton conductivity. Various recast Nafion composite membranes containing metal oxides were reported to exhibit high proton conductivity at low humidities and elevated temperatures [7–12]. This high conductivity is attributed to the enhanced water retention in the membrane by the metal oxides due to their hygroscopic property [7–12]. Doping the Nafion membrane with a heteropoly acid (HPA) has also been reported to achieve good proton conductivity at elevated temperatures [13–16]. HPAs typically exist in hydrated phases, in which the water molecules can form bridges between ionic clusters to facilitate proton transport even when Nafion is not fully hydrated at elevated temperatures [6].

Phosphotungstic acid (PWA) has the strongest acidity among the Keggin-type HPAs and water content as high as 10 wt% [15–18]. However, its widespread uses in PEMFCs is limited because of its solubility in water. It can gradually leach out from the membrane and reduce the catalytic activities of the electrocatalysts when it added in electrodes of PEMFCs. To address this issue, PWA was immobilized in Nafion membrane by connecting through SiO$_2$ [19–22]. These PWA/SiO$_2$/Nafion composite membranes exhibit an enhanced and stable performance at elevated temperatures and low humidities in PEMFCs [20–22] and direct methanol fuel cells [19].

In this work, we incorporate PWA/SiO$_2$ both in the Nafion membrane and the Nafion ionomer used in the electrodes of PEMFCs, following the same formulation and method reported by Mahreni et al. [21]. We hypothesize that equivalent proton (H$^+$) conductivity generated between the membrane and the electrodes by having identical ionomer in adjacent components of a membrane electrode assembly (MEA) would reduce the H$^+$ interfacial resistance between the membrane and electrodes to enhance the performance of a PEMFC. We also postulate that the anchored PWA is adequately embedded in the ionic channels of the Nafion ionomer, which would avoid the adsorption of PWA on the electrocatalysts, *i.e.*, the positioning of electrocatalysts [6,23]. In examining these two hypotheses, two types of MEAs are prepared for investigation: MEA-1 and MEA-2 have, respectively, PWA/SiO$_2$ both in the membrane and electrodes and in the membrane only. The two MEAs are characterized by the methods of potentiodynamic polarization, current interruption, and electrochemical impedance spectroscopy at various temperatures and relative humidities (RH) in a single PEMFC configuration. The measured ohmic resistances, open circuit voltages (OCVs), Tafel slopes, charge transfer time constants, etc. were analyzed and compared to verify the stated hypotheses.

2. Experimental

2.1. Materials for the preparation of the membrane and the electrodes

Nafion solution (5 wt%, DuPont), phosphotungstic acid (PWA, reagent grade, Sigma Aldrich), tetraethyl orthosilicate (TEOS, ≥99%, Sigma Aldrich), *N,N*-dimethylformamide (DMF, ACS reagent, ≥99.8%, Sigma Aldrich), sulfuric acid (H$_2$SO$_4$, ACS reagent, 95–98%, Sigma Aldrich), hydrogen peroxide (H$_2$O$_2$, 3% certified,

Fisher Scientific), platinum on carbon black (Pt/C, 40 wt%, Alfa Aesar), and isopropanol (certified, Fisher Chemicals) were used as received.

2.2. Preparation of the membranes

All membranes were cast in-house. The incorporation of immobilized PWA/SiO$_2$ in Nafion blend was carried out as reported by Mahreni et al. [21]. For the composite membranes with immobilized PWA/SiO$_2$, the weight ratio of Nafion:TEOS:PWA was 85.67:12.85:1.48. TEOS is the precursor of SiO$_2$ where TEOS converted into SiO$_2$ by hydrolysis in acidic medium. In membrane preparation, approximately 11 mL of the Nafion solution dried at room temperature, and reproduced 5 wt% Nafion solution was obtained by re-dissolving the dry Nafion in DMF. Separately, PWA was dissolved in de-ionized water, and TEOS was added and sonicated. It was then mixed with Nafion/DMF solution for over 6 h. After staying still for 24 h, the mixed solution was cast at 80 °C for 2 h and annealed for 10 h at 140 °C. The membrane without additives was cast following the same procedure. All prepared membranes were pre-treated by boiling in 3% H$_2$O$_2$ at 80 °C for 30 min to eliminate organic impurities, followed by boiling them in 0.5 M H$_2$SO$_4$ at 80 °C for 40 min to get rid of metallic impurities [13,24]. They were finally rinsed by de-ionized water to get rid of excess H$_2$SO$_4$. The thickness of the cast membranes was 48 ± 7 μm.

2.3. Preparation of the electrodes and MEAs

The catalyst inks were prepared by dispersing 40 wt% Pt/C electrocatalysts into the solution of de-ionized water, isopropanol, and Nafion or the Nafion with PWA/SiO$_2$ [25]. The volume ratio of water to isopropanol is 3:7 and the Nafion mass respect to the amount of carbon is 30 wt%. The Nafion with PWA/SiO$_2$ solution was prepared by mixing 5 wt% Nafion solution and PWA/TEOS aqueous solution with the same weight ratio of Nafion:TEOS:PWA as that of the composite membranes. The catalyst loadings for anode and cathode were approximately 0.2 mg$_{Pt}$ cm^{-2} and 0.4 mg$_{Pt}$ cm^{-2}, respectively.

The membrane electrode assemblies (MEAs) were prepared by directly spraying the catalyst inks on the cast membranes using an airbrush (Badger Airbrush: 155-1) [25]. The active areas of the MEAs were square and 5 cm^2. Two categories of assigned MEAs were prepared: MEA-1 contains immobilized PWA/SiO$_2$ both in the electrodes and membrane; MEA-2 contains immobilized PWA/SiO$_2$ only in the membrane.

2.4. Cell assembly and testing procedures

An MEA sandwiched between two gas diffusion layers was assembled in fuel cell hardware with serpentine flow channels. The performance of the MEA was evaluated on a fuel cell test station (890CL, Scribner Associates). The humidified hydrogen and oxygen gases were fed into the anode and cathode, respectively, at flow rates of 0.2 L min^{-1}. The cell was operated at temperatures of 80, 90, and 100 °C and at relative humidity (RH) of 50%, 75%, and 100% of the inlet gases. The polarization curves were potentiostatically recorded by the electrical load bank of the fuel cell test station. The electrochemical impedance spectroscopy (EIS) data were collected on a frequency response analyzer (Solartron 1260) coupled with an electrochemical potentiostat/galvanostat (Solartron SI 1287). The fuel cell was operated in a potentiostatic mode at a bias potential of 0.80 V vs. the anode, which is the dynamic hydrogen electrode (DHE) with relative stable potential. All potentials otherwise mentioned are versus this DHE. A small AC amplitude of 15 mV was superimposed on the fuel cell and the

frequency range is 0.1–4000 Hz [26,27]. The applied AC amplitude and frequency range do not significantly change the overall state of electrochemical system.

3. Results and discussion

The influences of immobilized PWA/SiO₂ additive in the electrodes on MEA performances were first evaluated by comparing the cell performances at different fuel cell operating temperatures and relative humidities (RH). Polarization curves recorded for MEA-1, having hybrid additive (PWA/SiO₂) in both the membrane and electrodes, and MEA-2, having PWA/SiO₂ only in the membrane. Both the MEAs were operated at temperatures of 80, 90, and 100 °C, and the RH were 100%, 75%, and 50% at each operating temperature. V–i curves at all operating settings are shown in Fig. 1. Under all the tested operating conditions, MEA-1 demonstrated better performances than MEA-2 by exhibiting higher current densities at same voltages. These results indicate that immobilized PWA/SiO₂ additive with Nafion ionomer in the electrodes can offer a cell performance advantage compared to neat Nafion. This superior performance might be due to the reduced interfacial protonic resistances between the membrane and electrodes due to the presence of identical ionomer in adjacent components in MEA thereby exhibiting overall lower cell resistance. In other words, identical ionomer in adjacent compartments conceivably helped to maintain equivalent ion transporting pace, and also assisted in reducing interfacial resistances towards ion transport through adjacent cell components.

Table 1

Current densities, i (mA cm^{-2}) at 0.70 V obtained for MEA-1 and MEA-2 at the fuel cell operating temperatures of 80, 90, and 100 °C and at RH of 100%, 75%, and 50%. The relative performance enhancement (RE, %) of the current densities is defined as the values of MEA-1 minus those of MEA-2 and divided by the values of MEA-2. The H₂ and O₂ were, respectively, fed into the anode and cathode at 0.2 L min^{-1} and atmospheric pressure. T_{FC} denotes the cell operating temperature and T_{RH} denotes the temperature set for both the anode and cathode humidifiers to attain the required RH.

Operating conditions		i values at 0.70 V (mA cm^{-2})		
T_{FC}/T_{RH} (°C/°C)	RH (%)	MEA-1	MEA-2	RE (%)
80/62	50	390 ± 34	180 ± 12	117
80/72	75	560 ± 37	320 ± 24	75
80/80	100	710 ± 53	520 ± 46	37
90/72	50	340 ± 23	210 ± 21	62
90/82	75	410 ± 26	280 ± 24	46
90/90	100	520 ± 47	400 ± 29	30
100/82	50	290 ± 18	150 ± 15	93
100/92	75	260 ± 21	240 ± 17	8
99/99	100	305 ± 29	300 ± 30	2

To quantify the superior performance, acquired current densities of MEA-1 and MEA-2 at 0.70 V (typical operating voltage) were tabulated in Table 1. The selection of potential in this evaluation is to understand the ohmic behavior changes among two MEAs and to understand the influences of ionomer in electrodes on cell performance. It can be clearly seen in Fig. 1c that MEA-1 has much higher current densities at 0.70 V than MEA-2 at 80 °C and
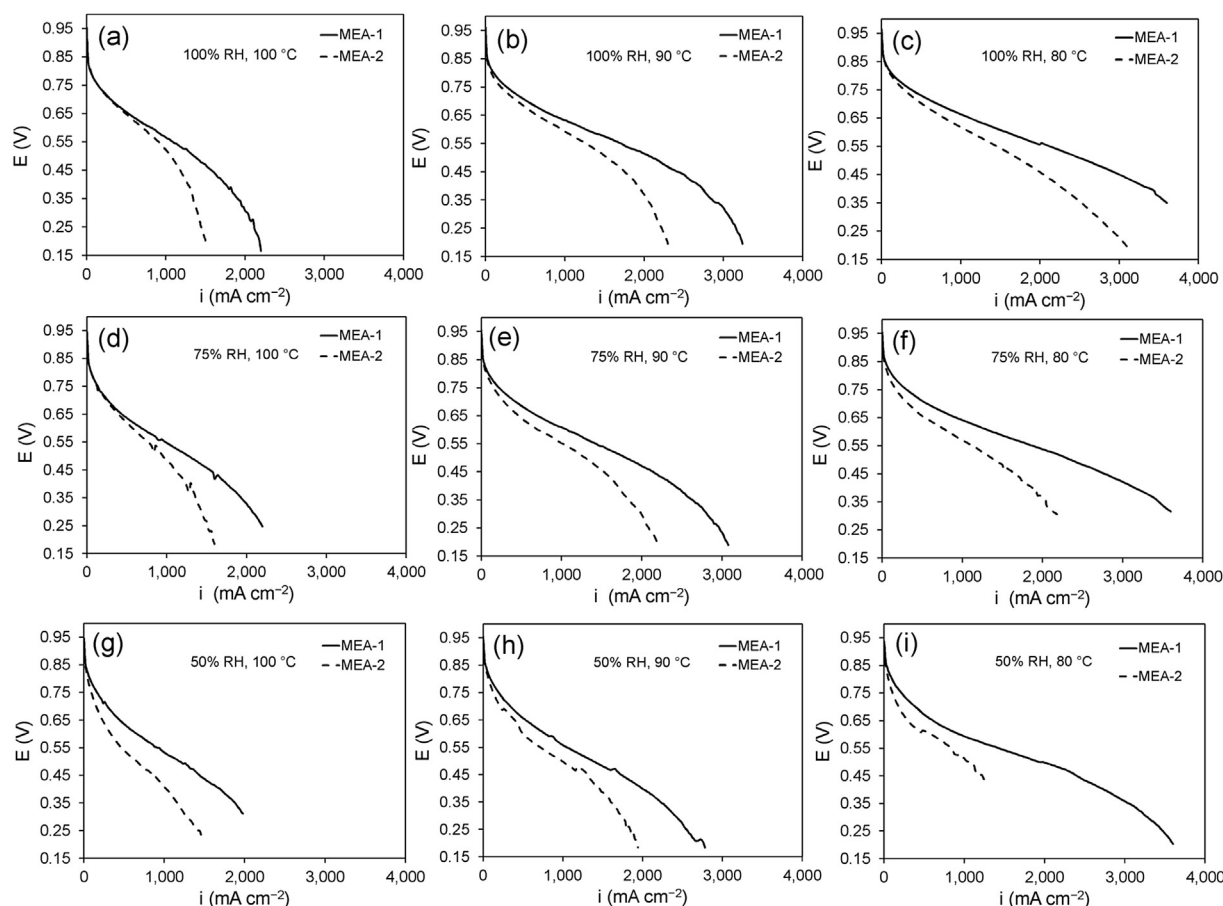

Fig. 1. Polarization curves recorded for MEA-1 and MEA-2 under the fuel cell operating temperatures of 80, 90, and 100 °C and at the RH of 100%, 75%, and 50%. H₂ and O₂ were fed into the anode and cathode respectively at 0.2 L min^{-1} and atmospheric pressure.

100% RH. Under these conditions, the Nafion ionomer in cells is well hydrated and set as the baseline in this study. The same observation was borne through at reduced humidities at 80 °C (Fig. 1c, f, and i). The additive is known to benefit the proton transport to Nafion ionomer at elevated temperatures and low RH [19–22]. The performance enhancement in MEA-1 partly can be ascribed to the reduced interfacial protonic resistances and increasing electrode ionic conductivity. As the cell temperature increases at 100% RH, both MEAs (Fig. 1a–c) have encountered in decreasing performances due to the decrease of the hydration levels of the Nafion ionomer across all components of the MEAs. Although the performance enhancements caused by the addition of immobilized PWA/SiO$_2$ are not significant at 100% RH and at 100 °C (in fact, identical up to 0.65 V), the enhanced performances for MEA-1 were quite visible at reduced humidities. These results strongly suggest that the enhanced performance of MEA-1 compare to MEA-2 as the RH decreases is attributable to having identical immobilized PWA in both electrodes and membrane (Table 1). It can be explained that the addition of immobilized PWA/SiO$_2$ in the electrodes along with similar additive in the membrane (MEA-1) helps to maintain the hydration of the Nafion ionomer in the electrodes at low RH as in membrane, by which better proton conductivities are obtained for the electrodes, leading to a better cell performance. The performance enhancement also implies that the addition of immobilized PWA/SiO$_2$ not only help on cell performance, also evidence that the electrocatalysts are not poisoned when PWA is anchored in ionomer (Nafion) channel in electrode matrix. To gain insight into the reasons of performance enhancement, polarization curves were analyzed in each of the three regions: activation, ohmic, and mass transfer regions [28]. As can be seen in Fig. 1, all the polarization curves do not show a sharp current decrease in the mass transfer region. Therefore, major focus has been given on the effect of PWA/SiO$_2$ in ion-transporting resistance within the electrode matrices.

The effectiveness of the immobilized PWA/SiO$_2$ in the electrodes can be studied by comparing the ohmic resistances of the MEAs under the different operating conditions. To eliminate the diffusion effects which are not as relevant, the ohmic resistances were measured at high cell voltage [29]. Fig. 2 compares the ohmic resistances at 0.80 V (R_Ω) of MEA-1 and MEA-2 as a function of temperature and RH, measured by using current interrupt (CI) technique and electrochemical impedance spectroscopy (EIS) [30]. Fig. 2a shows the plots of the $R_{\Omega,CI}$ values of both MEA-1 and MEA-2 obtained by CI technique at various temperatures and RHs. These plots certainly indicate that the $R_{\Omega,CI}$ values of both MEAs increase as RH decreases, which is consistent with the well-known property of Nafion ionomer, i.e., the proton conductivity decreases as the hydration level decreases. However, these results also show that MEA-1 has lower $R_{\Omega,CI}$ values than MEA-2. These lower $R_{\Omega,CI}$ values of MEA-1 at lower RH imply that of the water content of PWA eased proton conductivity within electrode matrices at lower set RH. Hence, the observed trend indicates that the additive in the electrodes does help to reduce the overall ohmic resistance of the MEA.

Although the values of $R_{\Omega,CI}$ did not change significantly with the increase in temperature when the RH was fixed at 100% for each of the MEAs, MEA-1 shows lower resistance. For example, the resistances of MEA-1 were 0.053 Ω cm^2 at 80 °C, 0.050 Ω cm^2 at 90 °C, and 0.052 Ω cm^2 at 100 °C, while the resistances for MEA-2 were 0.069 Ω cm^2 at 80 °C, 0.070 Ω cm^2 at 90 °C, and 0.067 Ω cm^2 at 100 °C. A clear distinction of $R_{\Omega,CI}$ values among test MEAs shown in Fig. 2 is that the MEA-1 does not change significantly with temperature at 75 and 50% RH. However, for MEA-2, the changes of $R_{\Omega,CI}$ with temperature are substantial with temperature at 75 and 50% RH. This provides an indication that the addition of the immobilized PWA/SiO$_2$ in the electrodes help to maintain the hydration level in the electrodes ionomer channels, which helps in increasing
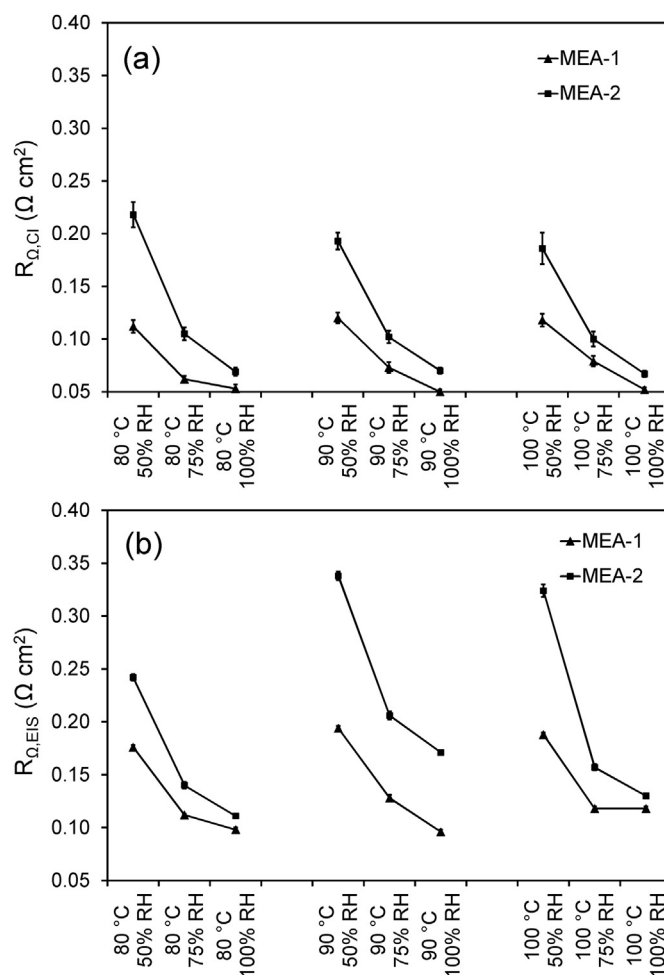

Fig. 2. Ohmic resistances at 0.80 V ($R_{0.8V}$) obtained by using (a) CI technique and (b) EIS for MEA-1 and -2 under the fuel cell operating temperatures of 80, 90, and 100 °C and at RH of 100%, 75%, and 50%. H$_2$ and O$_2$ were fed into the anode and cathode respectively at 0.2 L min^{-1} and atmospheric pressure.

the proton conductivity in electrodes and thus reducing the overall ohmic resistance of MEA-1. Comparing the result with baseline cell operating conditions, 80 °C and 100% RH, MEA-1 has a lower resistance compared to MEA-2. This difference is much smaller than those at other conditions, which suggests that the immobilized PWA/SiO$_2$ in the electrodes significantly reduced the interfacial ion transporting resistivity and facilitated better proton conductivity within the electrodes.

To further verify the critical parameter in this study, the ohmic resistances were also determined by the real impedance at high frequency using EIS technique. These results (Fig. 2b) exhibit the same trend as discussed above. Results obtained from both techniques strongly indicate that having PWA/SiO$_2$ nano-composite in both the membrane and electrodes of MEA-1 helped to reduce the interfacial ion transporting resistances between the membrane and electrodes, and also reduces the proton conducting resistances in the electrodes. The former reduction is less than the latter one and that the slight difference in the R_Ω values obtained by CI and EIS techniques is caused by the different perturbation of the system imposed by the two techniques.

Additionally, we compared the OCVs to verify the effects of the presence of immobilized PWA/SiO$_2$ in the electrodes on the activation loss of MEA-1. In general, the changes in OCV are due to organic or metallic impurities presented in an MEA, ECSA,

crossover of the fuel and oxidant, and occurring parasitic reactions, or combination of several factors thus mentioned [31–33]. Under identical experimental conditions with the same electrocatalysts, membrane, fabrication technique, and use of fuel and oxidant; lower OCV values are indicative of contamination of electrocatalysts by the PWA. Fig. 3 shows the OCV changes of MEA-1 and MEA-2 with varying temperature and RH. It can be seen that obtained OCV values for MEA-1 are higher than those for MEA-2 at almost all tested conditions, except for the conditions of 75% RH and 100% RH at 100 °C. At 75% RH, the OCVs of MEA-1 and MEA-2 are almost equal. At 100% RH, the OCV values are also within the experimental errors (Fig. 3). All the results clearly indicate that the addition of PWA in the electrodes in restrained condition does not hinder the electrocatalytic activity in MEAs. In other words, immobilized PWA/SiO$_2$ does not leach out from the Nafion ionomer clusters in the electrodes and membrane to poison the electrocatalysts.

Generally, Tafel slope, a kinetic parameter, is used to characterize the kinetics of the reactions in MEAs. A high value of Tafel slope implies sluggish kinetics. Tafel slopes were calculated from iR-free polarization curves, obtained by subtracting the $R_{\Omega,CI}$ from the polarization curves in Fig. 1 at current values ≤ 100 mA cm^{-2} [30]. Since the Tafel slope is mainly related to the activation overpotential, it is only determined at low current density. The obtained Tafel slopes of MEA-1 and MEA-2 were plotted as a function of temperature and RH in Fig. 4a. It can also be seen that MEA-1 has smaller Tafel slopes at all conditions. Again, these data strongly indicate that the addition of immobilized PWA/SiO$_2$ in the electrodes helps to reduce the activation overpotential than reducing catalytic activity. As mentioned earlier, the water content in PWA can maintain the necessary hydration level for transporting proton in the electrodes when external humidification is not accessible. This assertion is verified through the differences in Tafel slope of two MEAs with and without stabilized PWA at lower RH especially at 50% at 80, 90, and 100 °C although these values are not distinctly different in other conditions.

Activation losses (the critical parameter in this study) of MEAs can be further characterized by the charge transfer time constant ('τ'), the time taken for the transfer of charge between the electrode and the reacting species [34]. The 'τ' value expected to be low to minimize activation losses which is the product of charge transfer resistance (R_{ct}) and double layer capacitance (C_d) from EIS
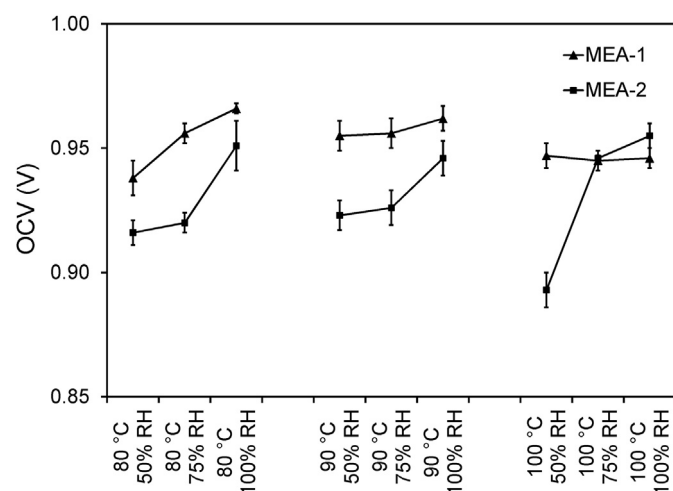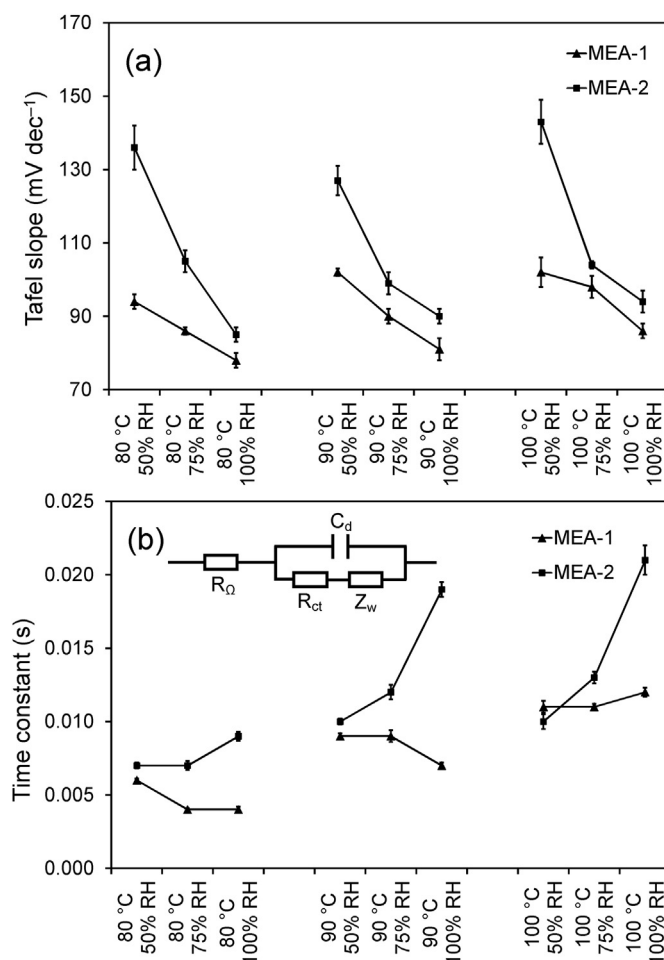

Fig. 4. (a) Tafel slope at $i < 100$ mA cm^{-2} from the experimentally recorded polarization data, and (b) charge transfer time constant from the EIS data of MEA-1 and -2 under the fuel cell operating temperatures of 80, 90, and 100 °C and at RH of 100%, 75%, and 50%. H$_2$ and O$_2$ were fed into the anode and cathode respectively at 0.2 L min^{-1} and atmospheric pressure. The inset in (b) is the equivalent electric circuit mimicking the fuel cell.

measurements. The equivalent circuit used to evaluate the impedance characteristics [35,36] of the fuel cell at different temperatures is given in the inset in Fig. 4b, in which R_Ω represents the ohmic resistance of the MEA; C_d is the double layer capacitance at the electrode-electrolyte interface; R_{ct} depicts the charge transfer resistance at the electrodes; and Z_w is known as the Warburg impedance, embodies the losses due to mass transfer. The 'τ' values for charge transfer against temperature and RH are presented in Fig. 4b. It can be seen that raising the temperature causes higher 'τ' as a result of increased charge transfer resistance owing to a reduced hydration level of Nafion ionomer in the electrodes [37]. This observation supports that the addition of immobilized PWA/SiO$_2$ in the electrodes helps to maintain the hydration level or improve the water retention of Nafion ionomer in the electrodes. By increasing RH, MEA-1 shows lowering of the time constant at 80 and 90 °C, which can be again related to the higher hydration level due to the immobilized PWA/SiO$_2$ in the electrodes.

4. Conclusions

Enhanced performance of an MEA has been successfully achieved by incorporating immobilized PWA/SiO$_2$ nano-composite both into the electrodes and membrane. It was verified that the

Fig. 3. OCV for MEA-1 and 2 under the fuel cell operating temperatures of 80, 90, and 100 °C and at RH of 100%, 75%, and 50%. H$_2$ and O$_2$ were fed into the anode and cathode respectively at 0.2 L min^{-1} and atmospheric pressure.

enhancement is mainly due to the enhanced hydration levels of the electrodes by the addition of immobilized PWA/SiO$_2$ in the electrodes, especially at elevated temperatures and low RH. The enhanced hydration of the electrodes not only increases the protonic conductivities in the electrodes but also promotes the charge transfer of the reactions at the electrodes. It was also proved that the protonic transport across the interfaces between the electrodes and membrane is improved compared to the MEA with the composite only in the membrane. However, this effect has less impact than the enhanced hydration levels of the electrodes on the performance enhancements of MEAs. In addition, the results demonstrated that immobilized PWA/SiO$_2$ in the electrodes does not have poisoning effects on the catalytic activities. The primary reason is that the PWA is adequately embedded in the ionic channels of the Nafion ionomer and does not interact with the electrocatalysts.

Acknowledgments

References

[1] P. Zegers, J. Power Sources 154 (2006) 497–502.
[2] K.D. Kreuer, J. Membr. Sci. 185 (2001) 29–39.
[3] T.A. Zawodzinski, J. Davey, J. Valerio, S. Gottesfeld, Electrochim. Acta 40 (1995) 297–302.
[4] A. Chandan, M. Hattenberger, A. El-kharouf, S. Du, A. Dhir, V. Self, B.G. Pollet, A. Ingram, W. Bujalski, J. Power Sources 231 (2013) 264–278.
[5] J. Zhang, Z. Xie, J. Zhang, Y. Tang, C. Song, T. Navessin, Z. Shi, D. Song, H. Wang, D.P. Wilkinson, Z.-S. Liu, S. Holdcroft, J. Power Sources 160 (2006) 872–891.
[6] V. Ramani, H.R. Kunz, J.M. Fenton, J. Membr. Sci. 232 (2004) 31–44.
[7] M. Watanabe, H. Uchida, Y. Seki, M. Emori, P. Stonehart, J. Electrochem. Soc. 143 (1996) 3847–3852.
[8] M. Watanabe, H. Uchida, M. Emori, J. Phys. Chem. B 102 (1998) 3129–3137.
[9] P.L. Antonucci, A.S. Aricò, P. Cretì, E. Ramunni, V. Antonucci, Solid State Ionics 125 (1999) 431–437.
[10] A.S. Aricò, V. Baglio, A. Di Blasi, P. Creti, P.L. Antonucci, V. Antonucci, Solid State Ionics 161 (2003) 251–265.
[11] H. Uchida, Y. Ueno, H. Hagihara, M. Watanabe, J. Electrochem. Soc. 150 (2003) A57–A62.
[12] G. Alberti, M. Casciola, E. Ramunni, R.O. Jacobo, Nuvera Fuel Cells Europe S.r.l. de Nora Electrodi S.p.A, US Patent, US7144652 B2, 2006.
[13] S. Malhotra, R. Datta, J. Electrochem. Soc. 144 (1997) L23–L26.
[14] B. Tazi, O. Savadogo, Electrochim. Acta 45 (2000) 4329–4339.
[15] A. Goñi-Urtiaga, D. Presvytes, K. Scott, Int. J. Hydrogen Energy 37 (2012) 3358–3372.
[16] J.L. Lu, Q.H. Fang, S.L. Li, S.P. Jiang, J. Membr. Sci. 427 (2013) 101–107.
[17] O. Nakamura, I. Ogino, T. Kodama, Solid State Ionics 3–4 (1981) 347–351.
[18] M. Misono, Catal. Rev. Sci. Eng. 29 (1987) 269–321.
[19] P. Staiti, A.S. Aricò, V. Baglio, F. Lufrano, E. Passalacqua, V. Antonucci, Solid State Ionics 145 (2001) 101–107.
[20] Z.-G. Shao, P. Joghee, I.M. Hsing, J. Membr. Sci. 229 (2004) 43–51.
[21] A. Mahreni, A.B. Mohamad, A.A.H. Kadhum, W.R.W. Daud, S.E. Iyuke, J. Membr. Sci. 327 (2009) 32–40.
[22] Z.-G. Shao, H. Xu, M. Li, I.M. Hsing, Solid State Ionics 177 (2006) 779–785.
[23] Y. Wu, X. Ye, X. Yang, X. Wang, W. Chu, Y. Hu, Ind. Eng. Chem. Res. 35 (1996) 2546–2560.
[24] J.-C. Lin, C.-M. Lai, F.-P. Ting, S.-D. Chyou, K.-L. Hsueh, J. Appl. Electrochem. 39 (2009) 1067–1073.
[25] A.B. Bose, R. Shaik, J. Mawdsley, J. Power Sources 182 (2008) 61–65.
[26] F. Chen, B. Mecheri, A. D'Epifanio, E. Traversa, S. Licoccia, Fuel Cells 10 (2010) 790–797.
[27] L. Birry, C. Bock, X. Xue, R. McMillan, B. MacDougall, J. Appl. Electrochem. 39 (2009) 347–360.
[28] M.V. Williams, H.R. Kunz, J.M. Fenton, J. Electrochem. Soc. 152 (2005) A635–A644.
[29] T.E. Springer, T.A. Zawodzinski, M.S. Wilson, S. Gottesfeld, J. Electrochem. Soc. 143 (1996) 587–599.
[30] K.R. Cooper, M. Smith, J. Power Sources 160 (2006) 1088–1095.
[31] D. Bevers, M. Wöhr, K. Yasuda, K. Oguro, J. Appl. Electrochem. 27 (1997) 1254–1264.
[32] K.T. Adjemian, S.J. Lee, S. Srinivasan, J. Benziger, A.B. Bocarsly, J. Electrochem. Soc. 149 (2002) A256–A261.
[33] S.A. Vilekar, R. Datta, J. Power Sources 195 (2010) 2241–2247.
[34] C. Brunetto, A. Moschetto, G. Tina, Electr. Pow. Syst. Res. 79 (2009) 17–26.
[35] N. Wagner, J. Appl. Electrochem. 32 (2002) 859–863.
[36] X. Yuan, H. Wang, J. Colin Sun, J. Zhang, Int. J. Hydrogen Energy 32 (2007) 4365–4380.
[37] J. Zhang, Y. Tang, C. Song, Z. Xia, H. Li, H. Wang, J. Zhang, Electrochim. Acta 53 (2008) 5315–5321.